Surface Engineering of Glazing Materials and Structures using Plasma Processes

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Motivation: Plasma and Related Technologies

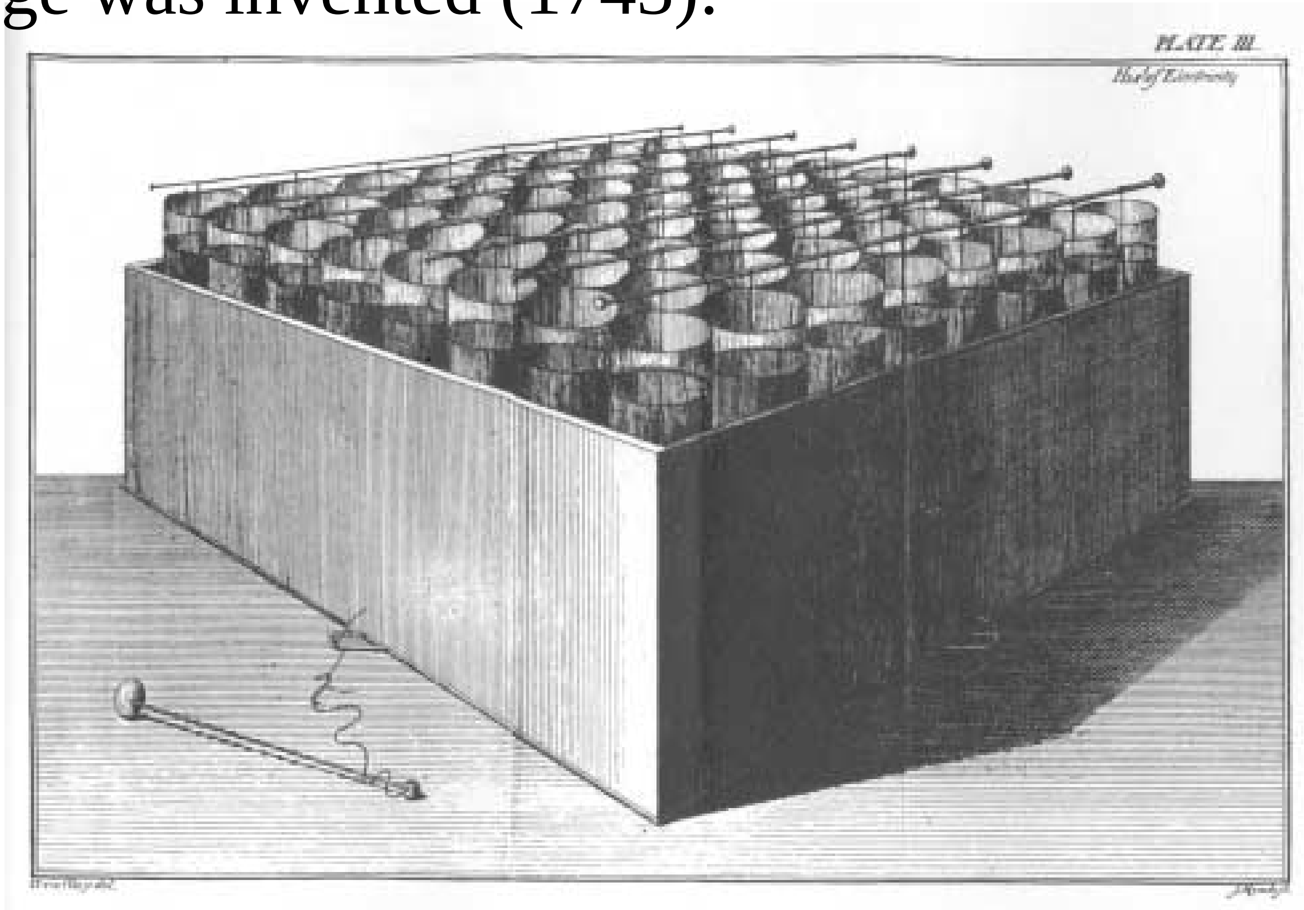
- a wake up call: energy crisis in early 1970s led to first low-emissivity coatings (e.g. thin gold films)
- development of (static) low-E and solar control: stack with Ag films and antireflection coatings
- in 1980s: first small-area switchable (dynamic) devices
  - no quick development to commercial windows: technical difficulties and related costs were underestimated
- in 1980-90s: important improvements in sputtering, plasma technology and diagnostics,materials characterization, process controls, computer simulation
- late 1990s: explosive growth of nanotechnology

Surface and Coatings Engineering with Plasmas

- Advantages of plasmas in processing:
  - in-situ etching (cleaning) of substrate
  - activation of film-forming species lead to enhanced control of stoichiometric composition
  - kinetic energy of ions can be enhanced and controlled by applied potentials (energetic condensation): denser films
  - potential energy of condensing species is enhanced: local heating, smoother films
  - many free process parameters
- Disadvantages:
  - Vacuum process: high cost
  - relatively complicated, not always understood
  - (too) many free process parameters

Plasma Coating on Glass: The Very First Steps

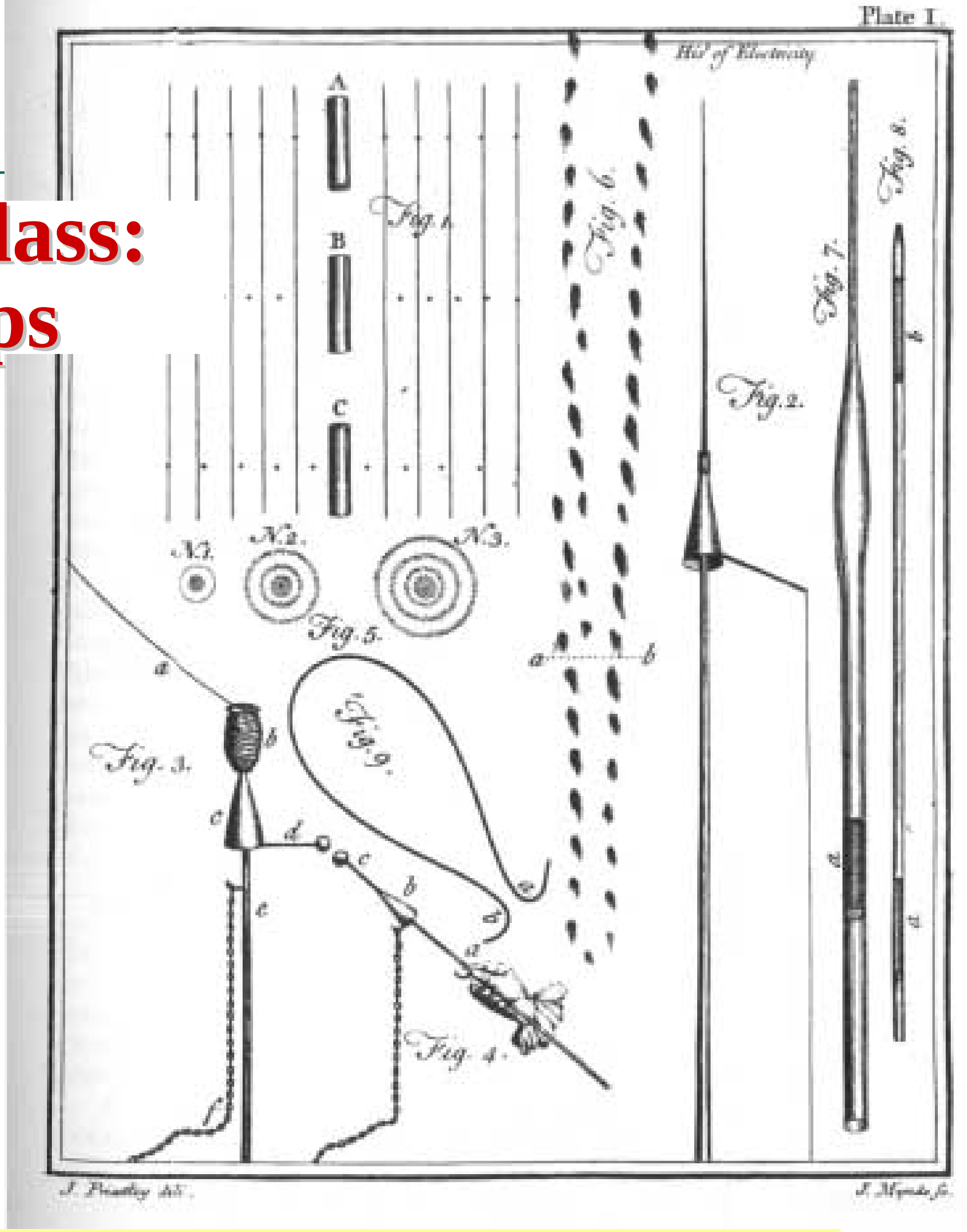
- Discharges and Plasmas made as soon as energy storage was invented (1743):



A. Anders, *IEEE Trans. Plasma Sci.* **31** (2003) August issue, in print.

Plasma Coating on Glass: The Very First Steps

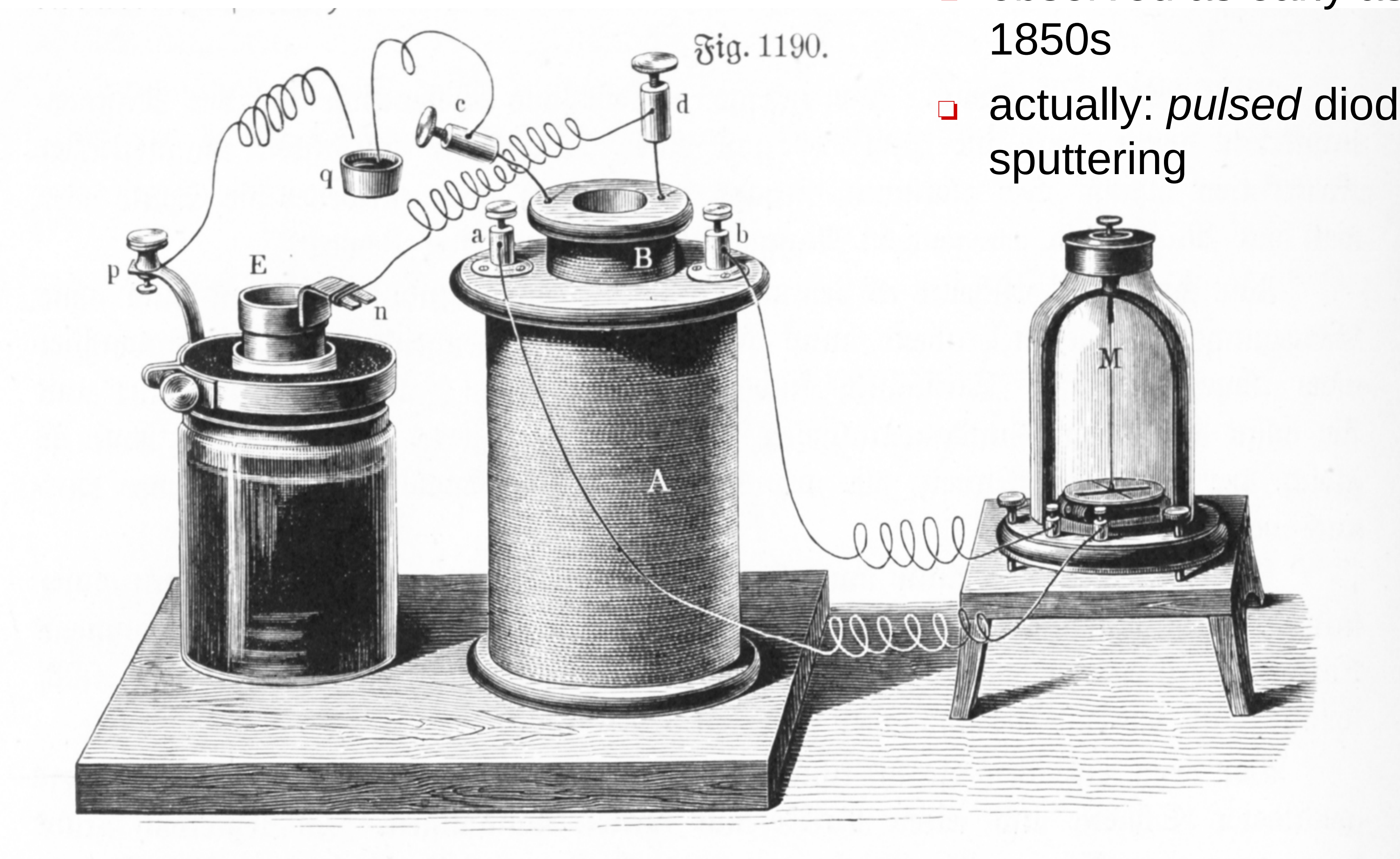
- Priestley 1766: first cathodic arc coatings of oxides on glass



A. Anders, *IEEE Trans. Plasma Sci.* **31** (2003) August issue, in print.

Development of Sputtering

- **Diode Sputtering**
  - observed as early as in 1850s
  - actually: *pulsed* diode sputtering



Development of Sputtering

- **Magnetron sputtering**: Enhancement of the plasma density at the target by a magnetic field;
- **Unbalanced magnetron sputtering**: the magnetic field lines are not closed at the target, thus flow to the substrate is enhanced;
- **Reactive sputtering**: use of reactive gas in sputter gas mixture, deposition of compound films;
- **RF sputtering**: insulating targets can be used;
- **Dual or twin magnetron sputtering**: Two targets working with alternating current, often at medium frequency, the problem of the "disappearing anode" is solved

Development of Sputtering

- **Dual or twin magnetron sputtering**: Two targets working with alternating current (**AC**), often at medium frequency (**MF**), the problem of the "disappearing anode" is solved
- **Hollow-cathode gas flow sputtering**: The to be sputtered material has hollow cathode shape, sputter gas flows through it and facilitates transport of material to substrate
- **Ionized sputtering** (**i-PVD**): Additional plasma ionization, usually by **RF**-fields between magnetron and substrate
- pulsed sputtering, especially **high power pulsed magnetron sputtering** (**HPPMS**): Power to magnetron is pulsed at a level > 100 x usual power

Development of Sputtering

- **Rotating magnetron sputtering**, often with cylindrical cathodes: target utilization is greatly improved;
- **High-Pulsed power magnetron sputtering**: During pulses, the current (hence power) is increased by orders of magnitude; the degree of ionization and particle energy can be greatly enhanced.

Pulsed Sputtering

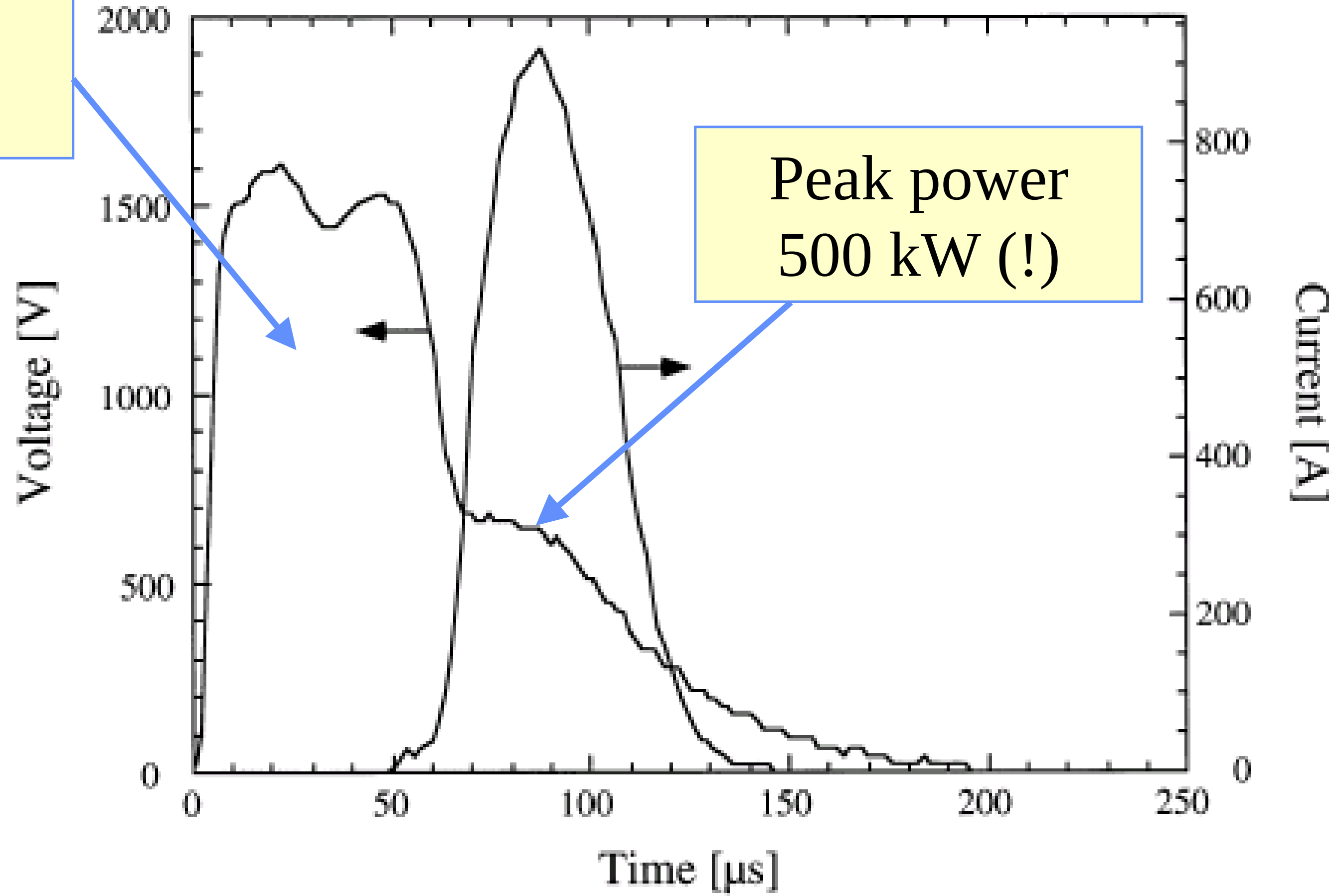
- Proposed by Kouznetsov and co-workers in late 1990s
- use of traditional sputter magnetron
- increase power during pulses by > 2 orders of magnitude
- average power is within acceptable level by using low duty cycle
- observe increased degree of ionization

Voltage-Current Waveform for Pulsed Sputtering

Cu target, 65 mPa Ar

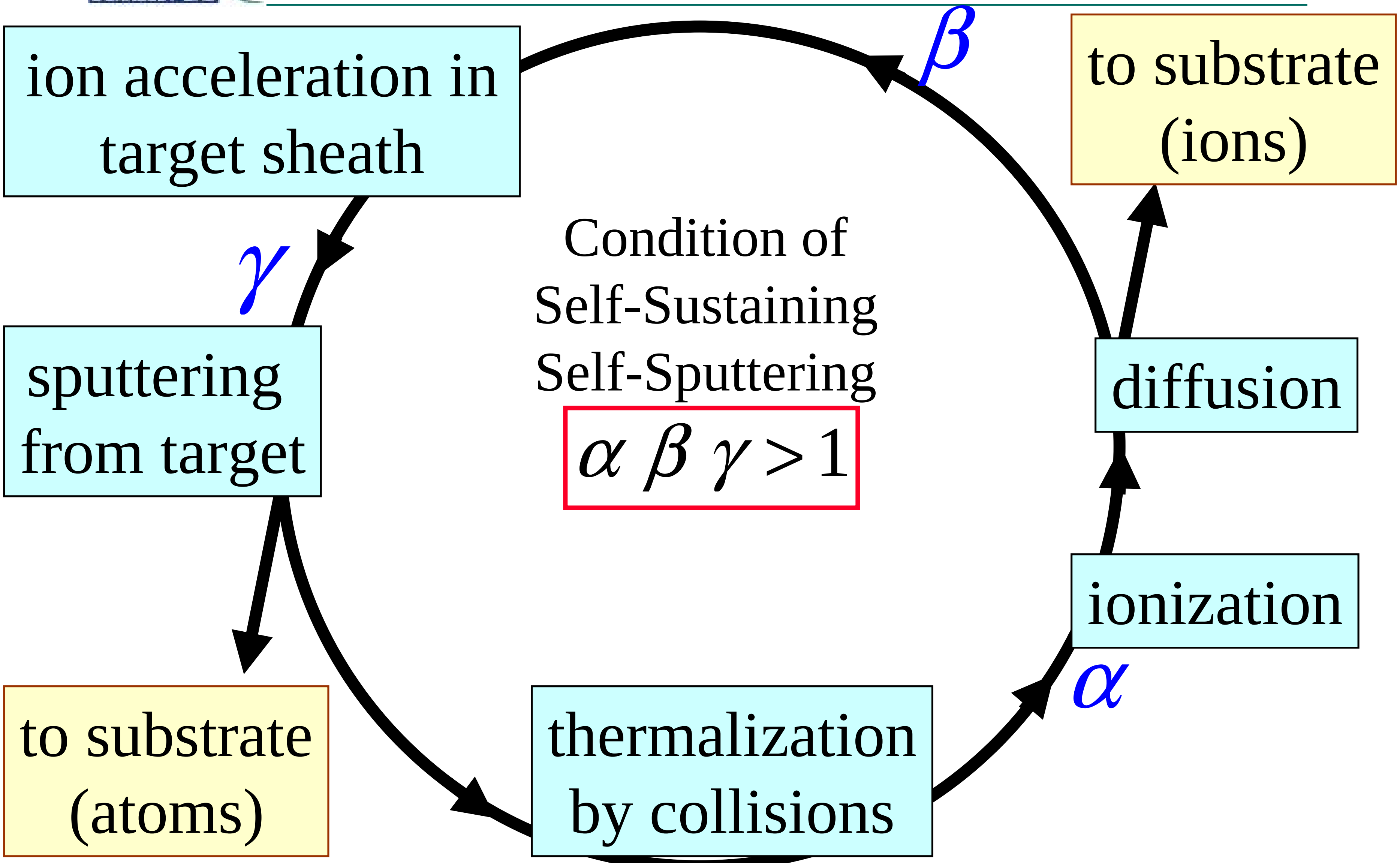
(no simmer discharge)

Peak power 500 kW (!)

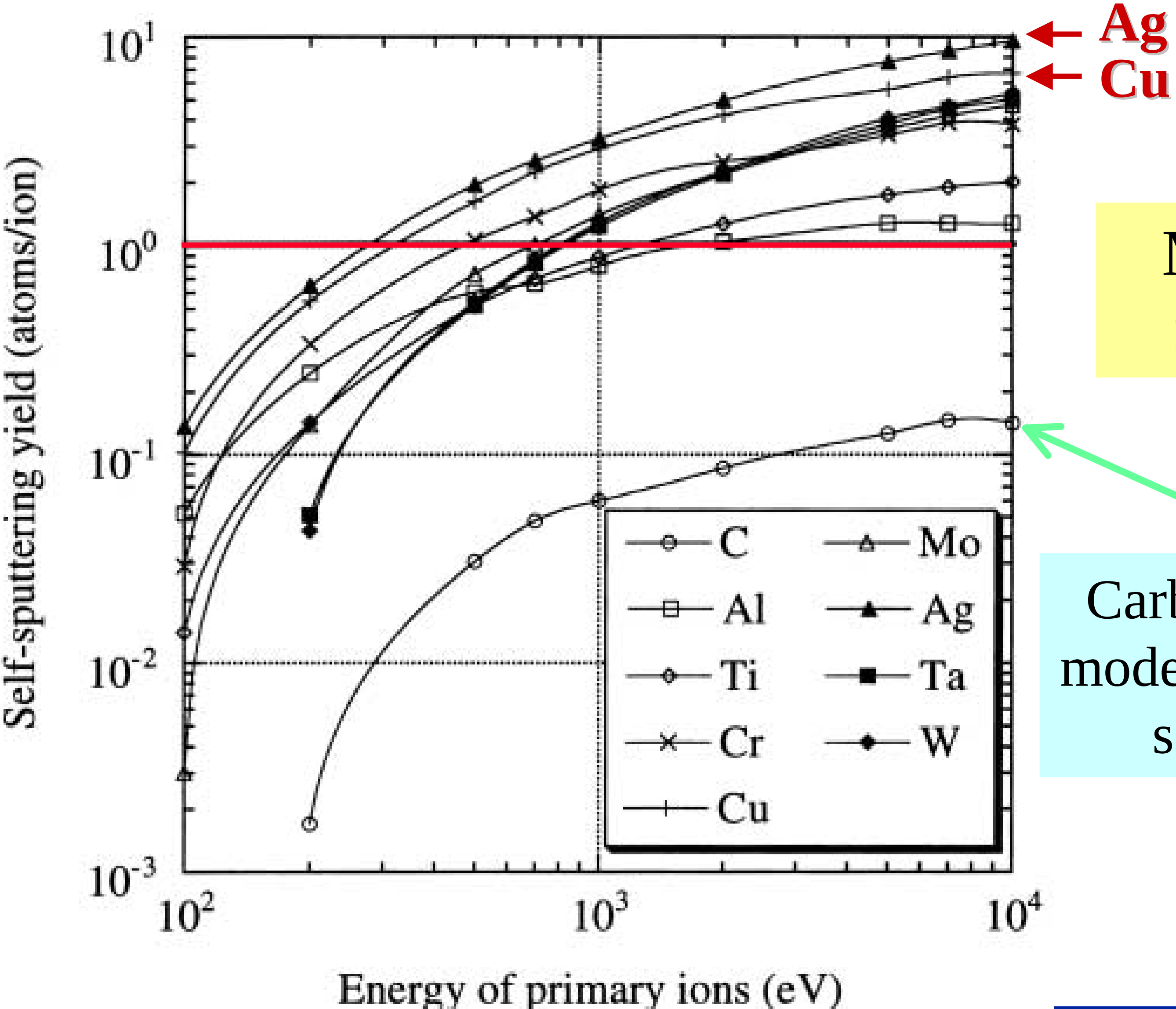


V. Kouznetsov, et al., *Surf. Coat. Technol.* **122**, 290-293 (1999)

Self-Sustained Self-Sputtering



Self-Sputter Yield

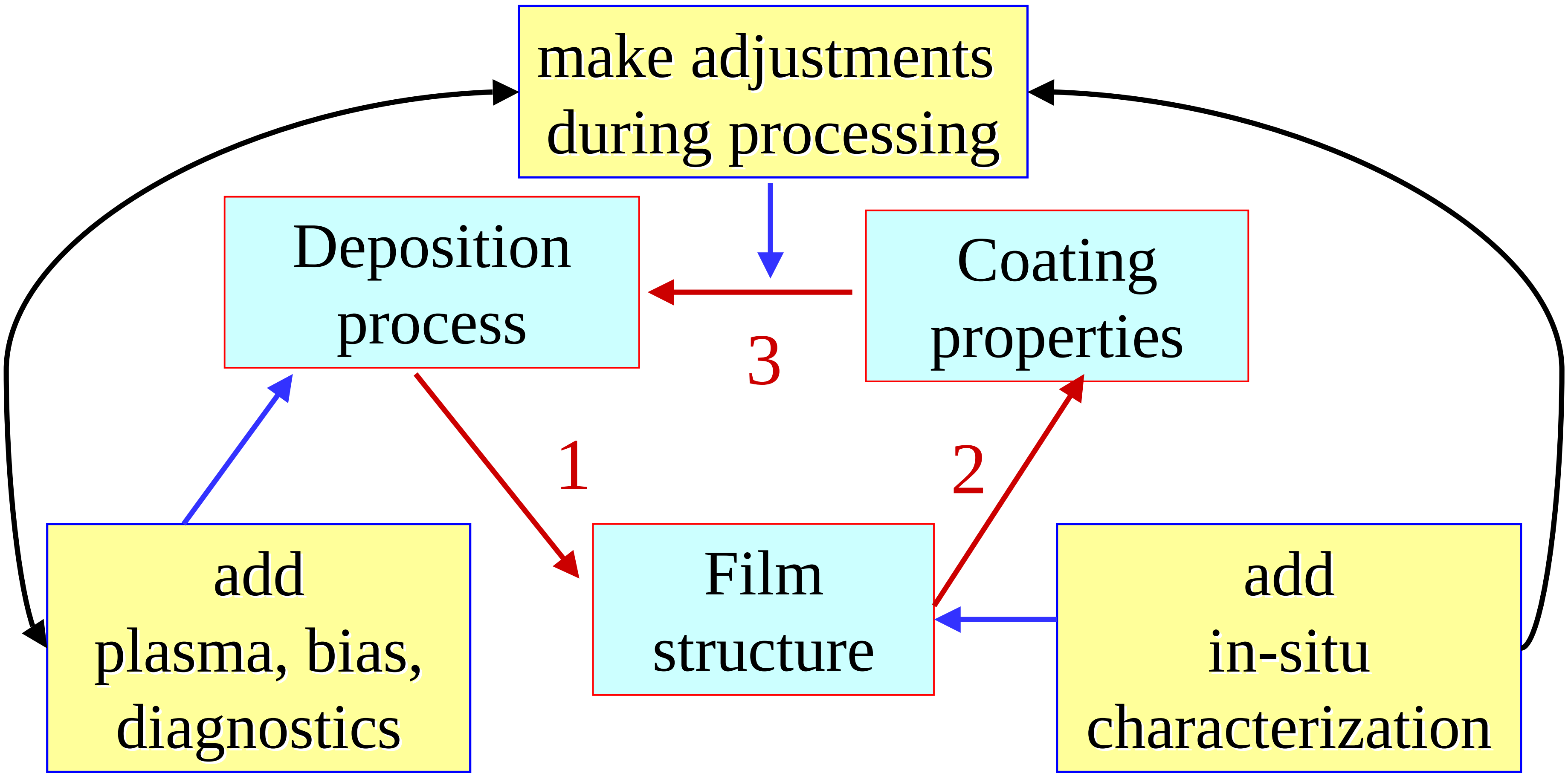


Monte Carlo Simulations

Carbon cannot go in mode of self-sustained self-sputtering

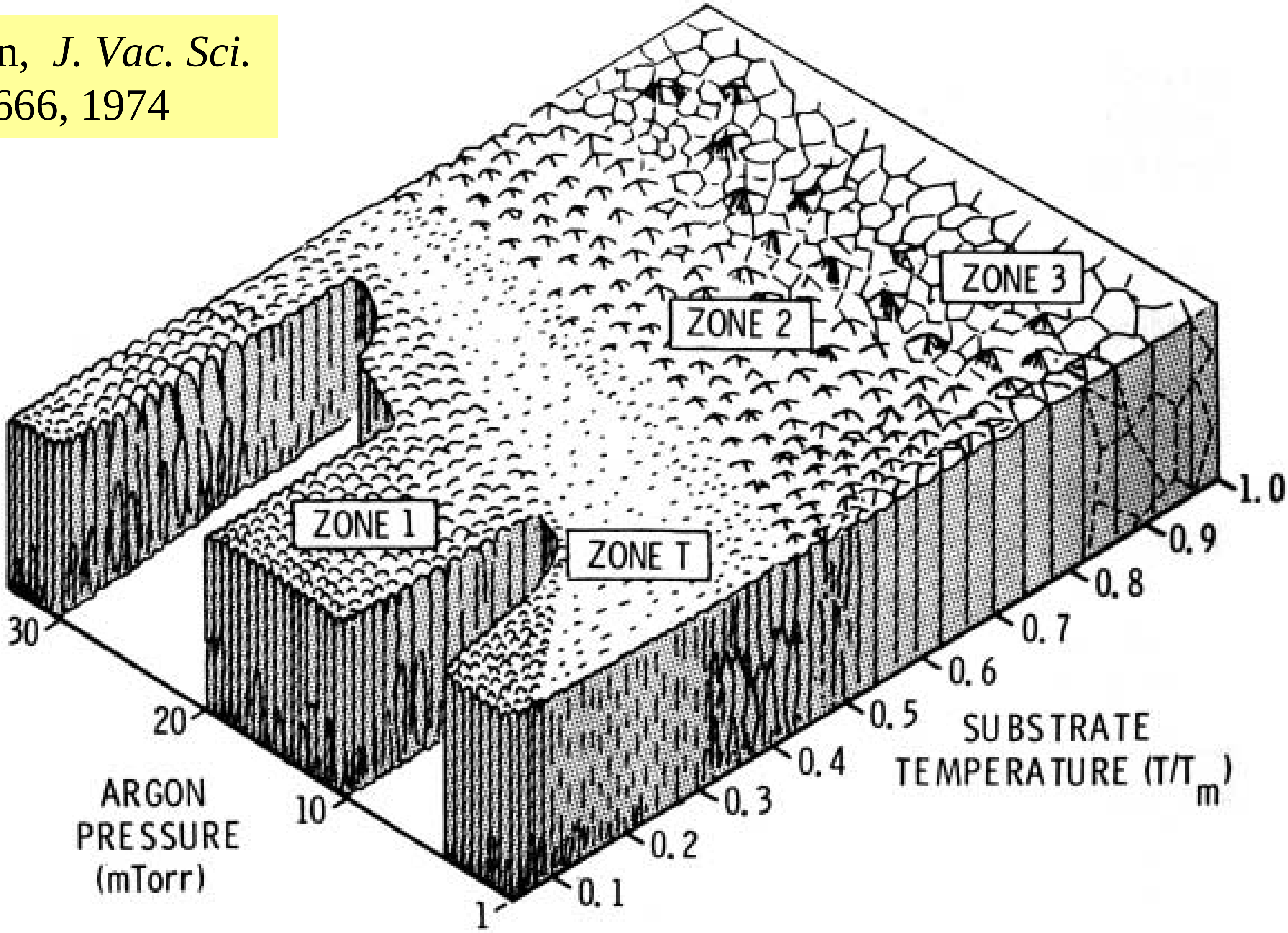
Closing the Feedback Loop

generic, but not trivial:



Thorton Zone Diagram

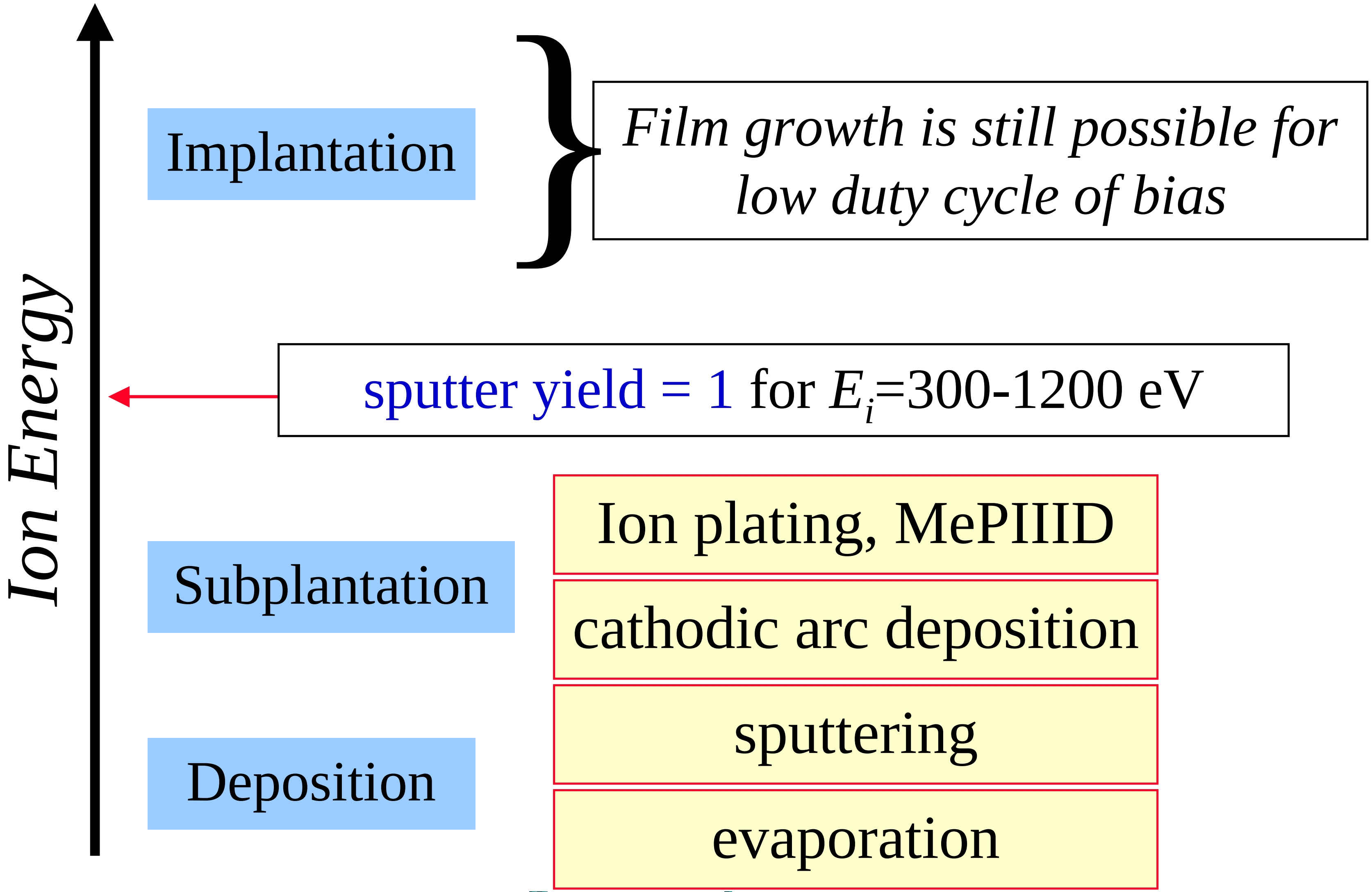
J. A. Thornton, *J. Vac. Sci. Technol.* **11**, 666, 1974



Film Growth and Properties

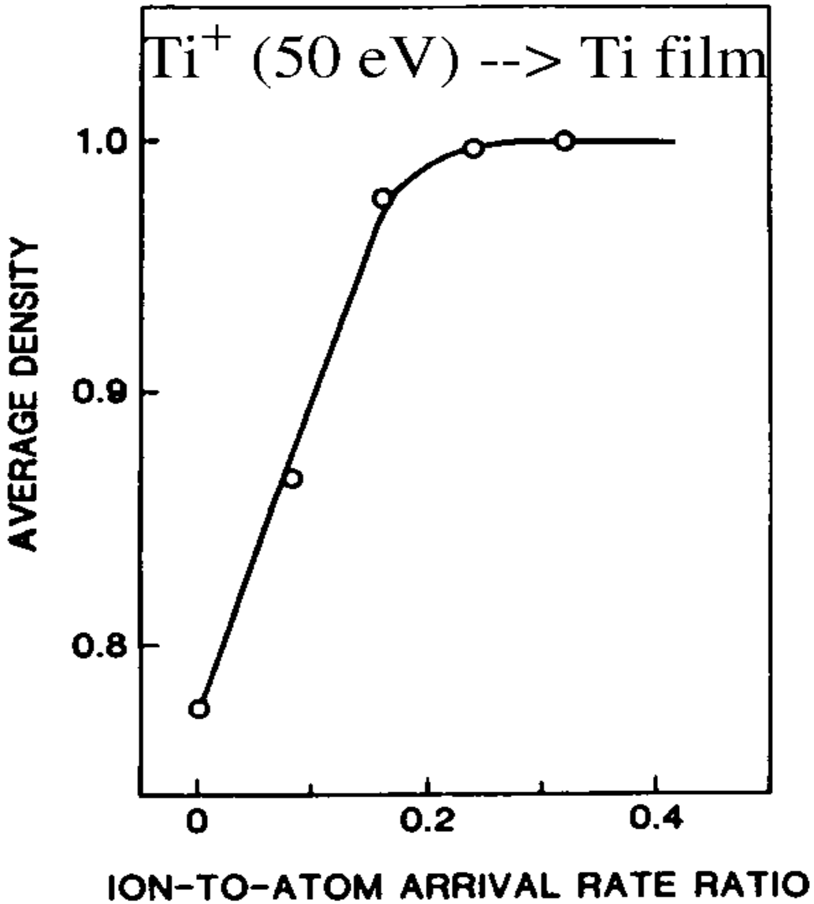
- Growth Modes: Layer-by-Layer versus Islands
- Equilibrium: Substrate material and temperature determines growth
- when kinetic factors included: growth can occur far from thermodynamic equilibrium
- examples for kinetically driven deposition ("energetic condensation"):
  - i-PVD, HPPMS
  - filtered cathodic arc deposition

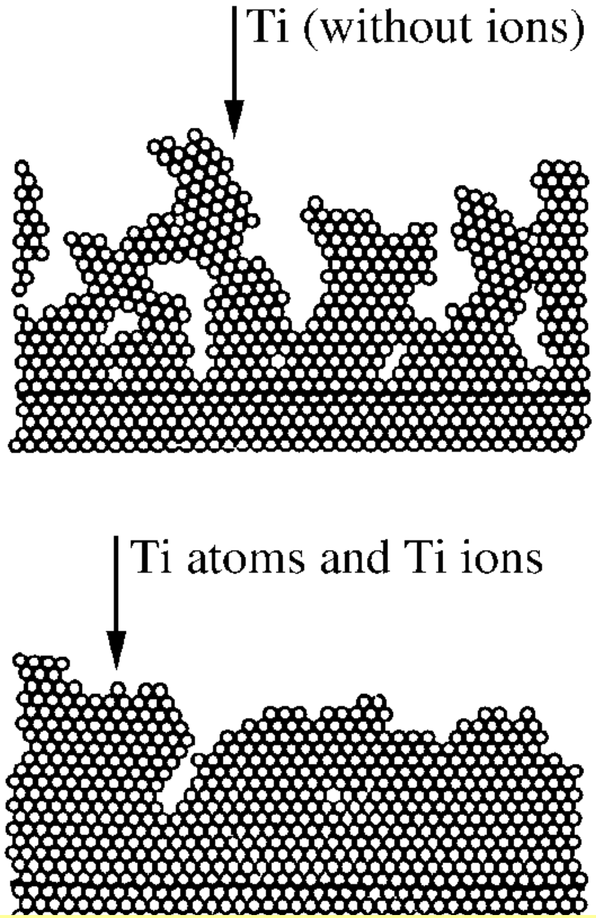
Energetic Relation Between Implantation and Deposition Processes



Effect of self-ion bombardment on film microstructure

- Densification of Ti film by Ti ions (self-ion assistance) at room temperature

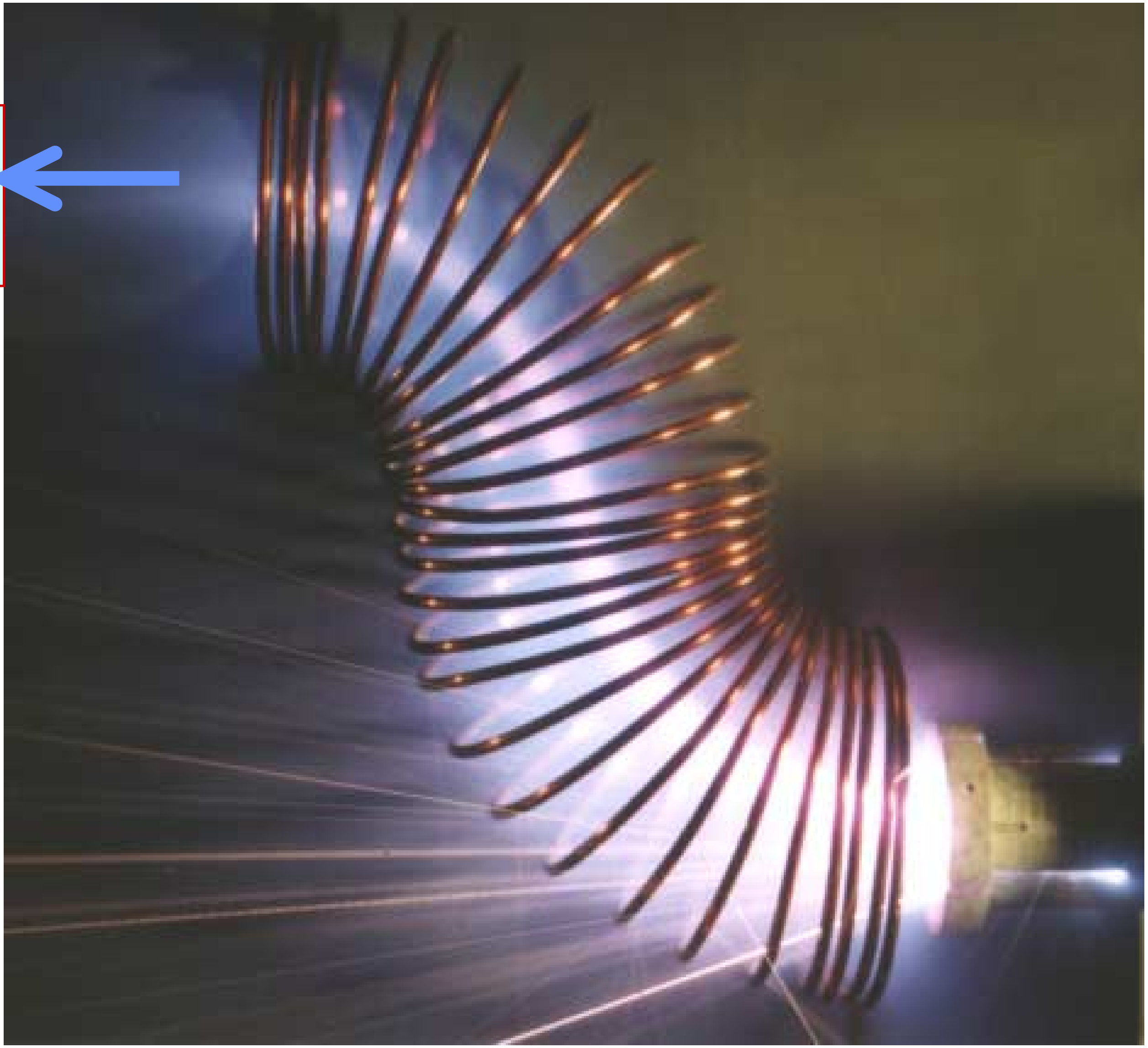




Martin et al. *JVST* **5** (1987) 22

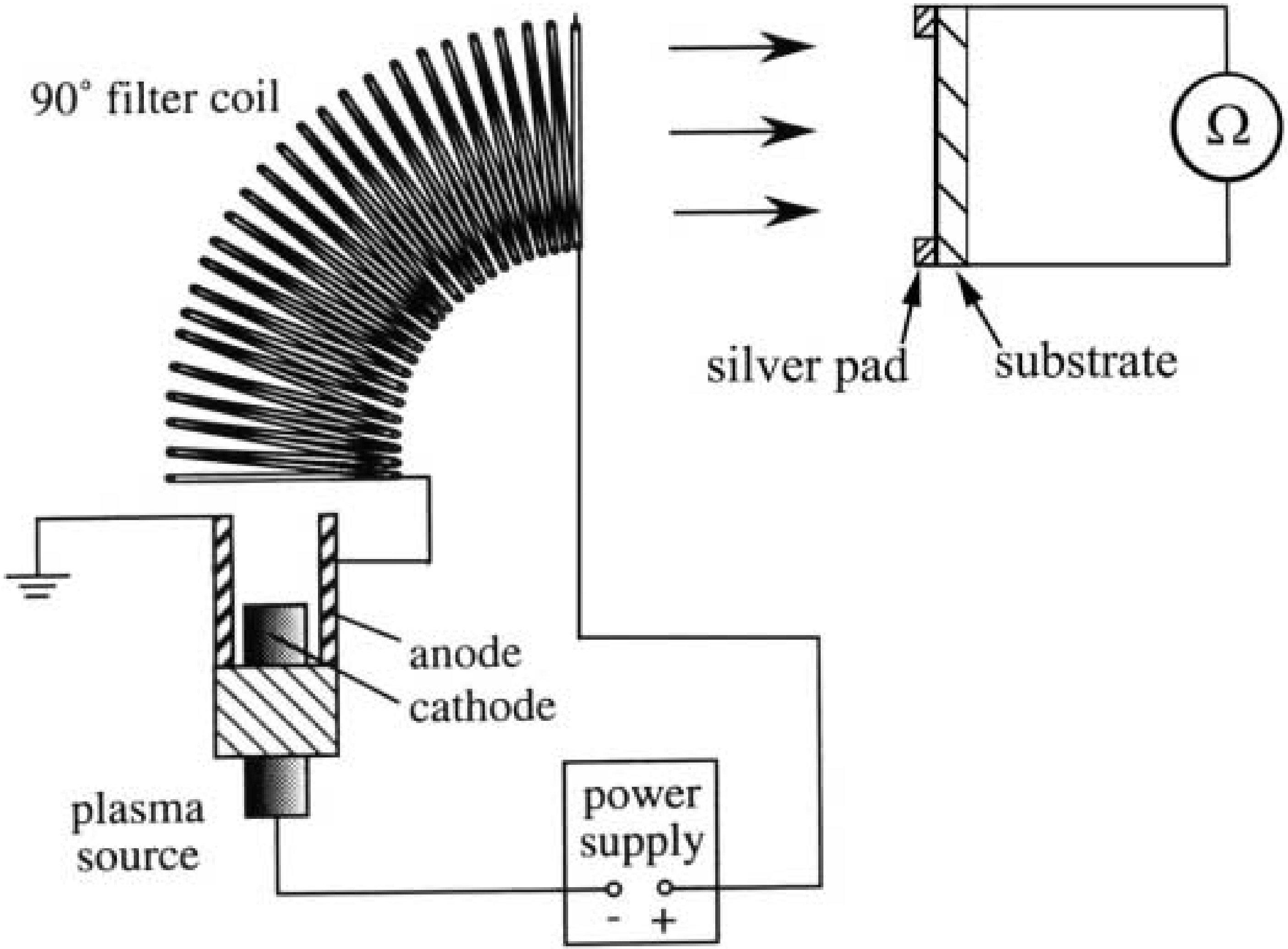
Example: Energetic Condensation using Filtered Cathodic Arcs

streaming, clean metal plasma



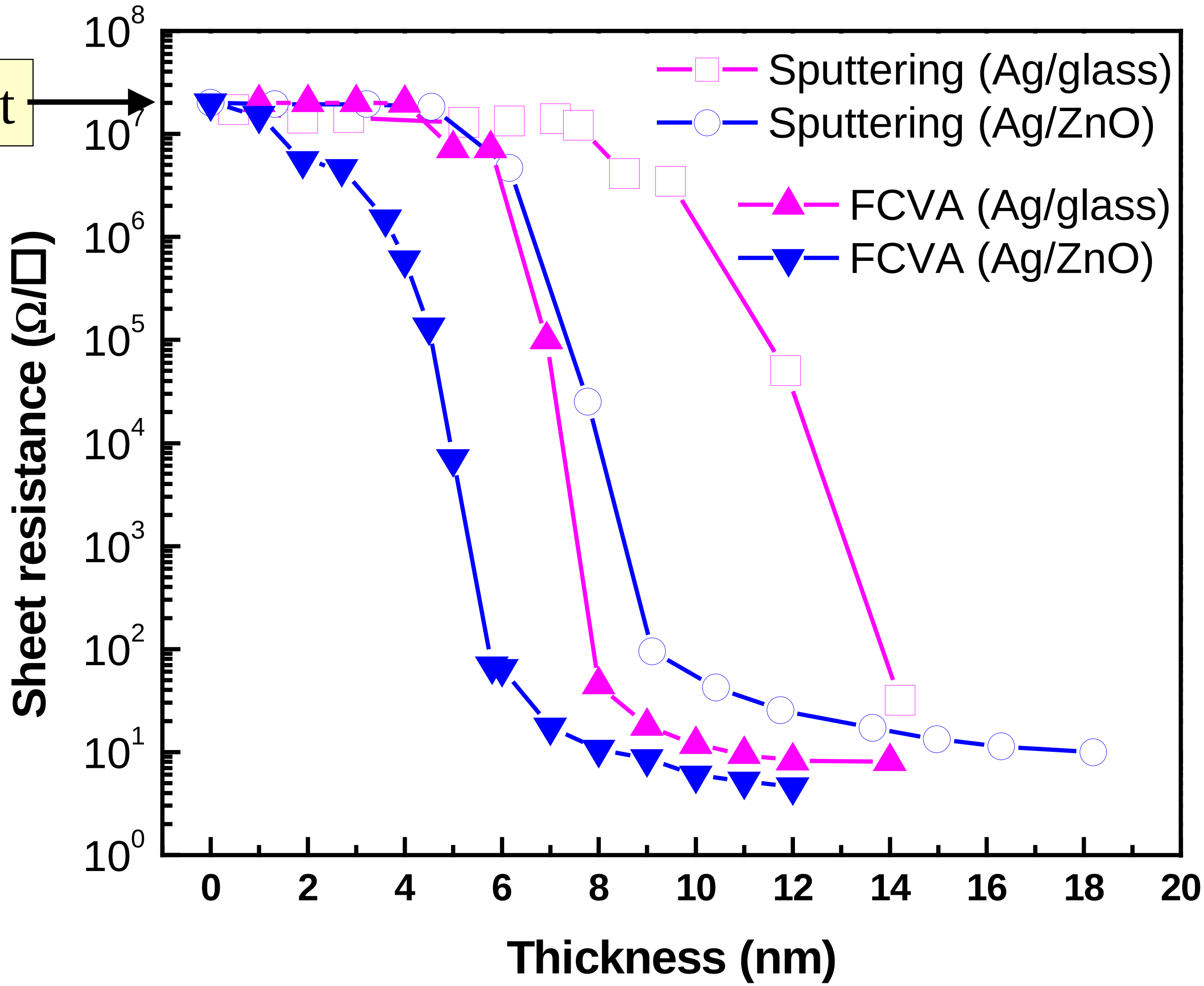
- ta-C
- metal films
  e.g. Ag films
- compounds

Coalescence and Post-Deposition Dynamics of Ultrathin Silver Film



Deposition of Ultrathin Silver Films

limit of instrument



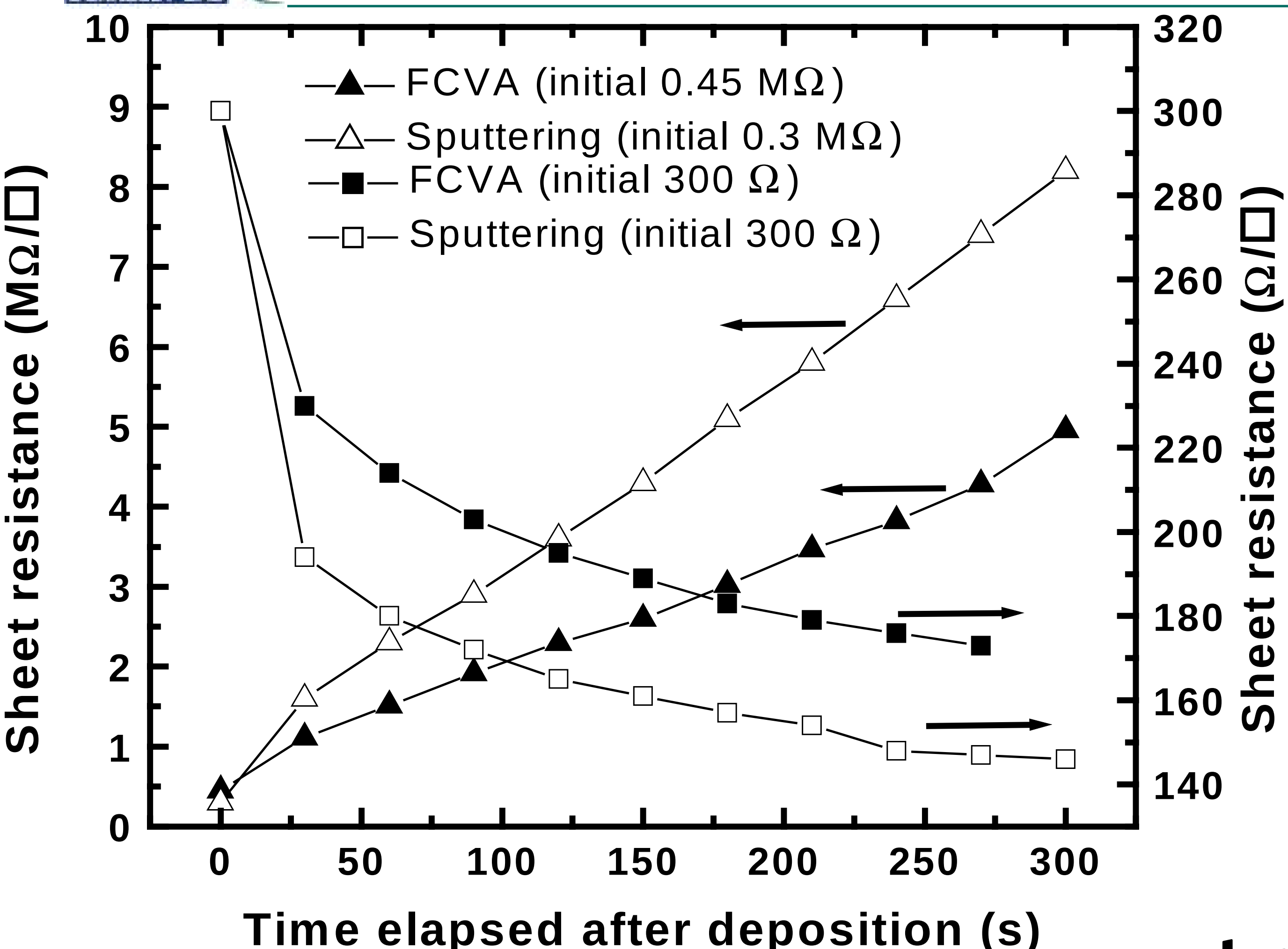
- in-situ
- seconds after deposition

E. Byon et al., *Appl. Phys. Lett.* **82** (2003) 1634

Post-Deposition Dynamics

- thermodynamic forces may can lead to diffusion and rearrangement,
- lowering the total energy of system, including
  - film atom - substrate atom interaction energy
  - film atom - film atom interaction energy
  - strain energy
- thermodynamic forces are the stronger the further the system is from thermodynamic equilibrium
- higher temperature promotes system to move to equilibrium

Post-Deposition Dynamics

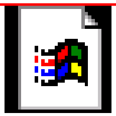


nominal room temperature!

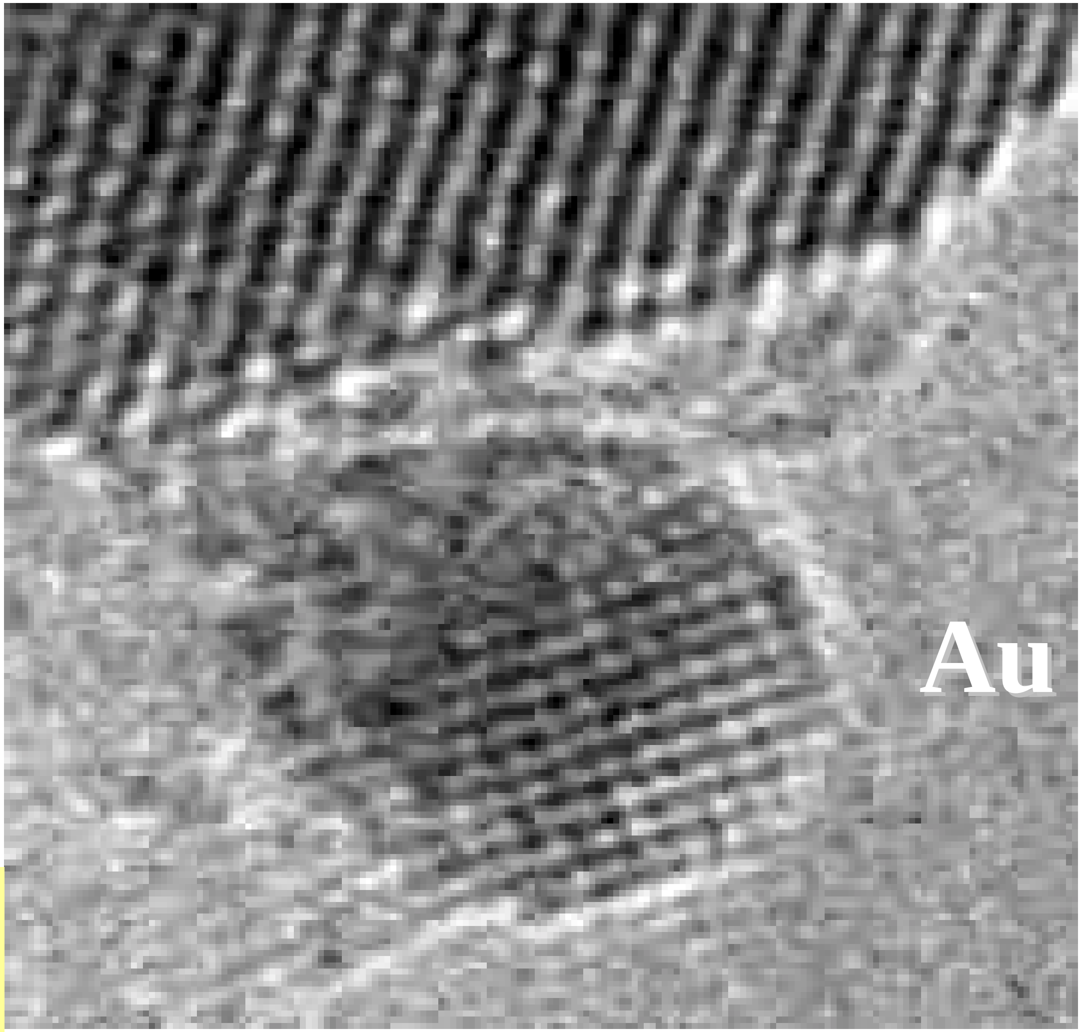
E. Byon et al., *Appl. Phys. Lett.* **82** (2003) 1634

Coalescence

- thermal motion and island growth by continued deposition lead to coalescence



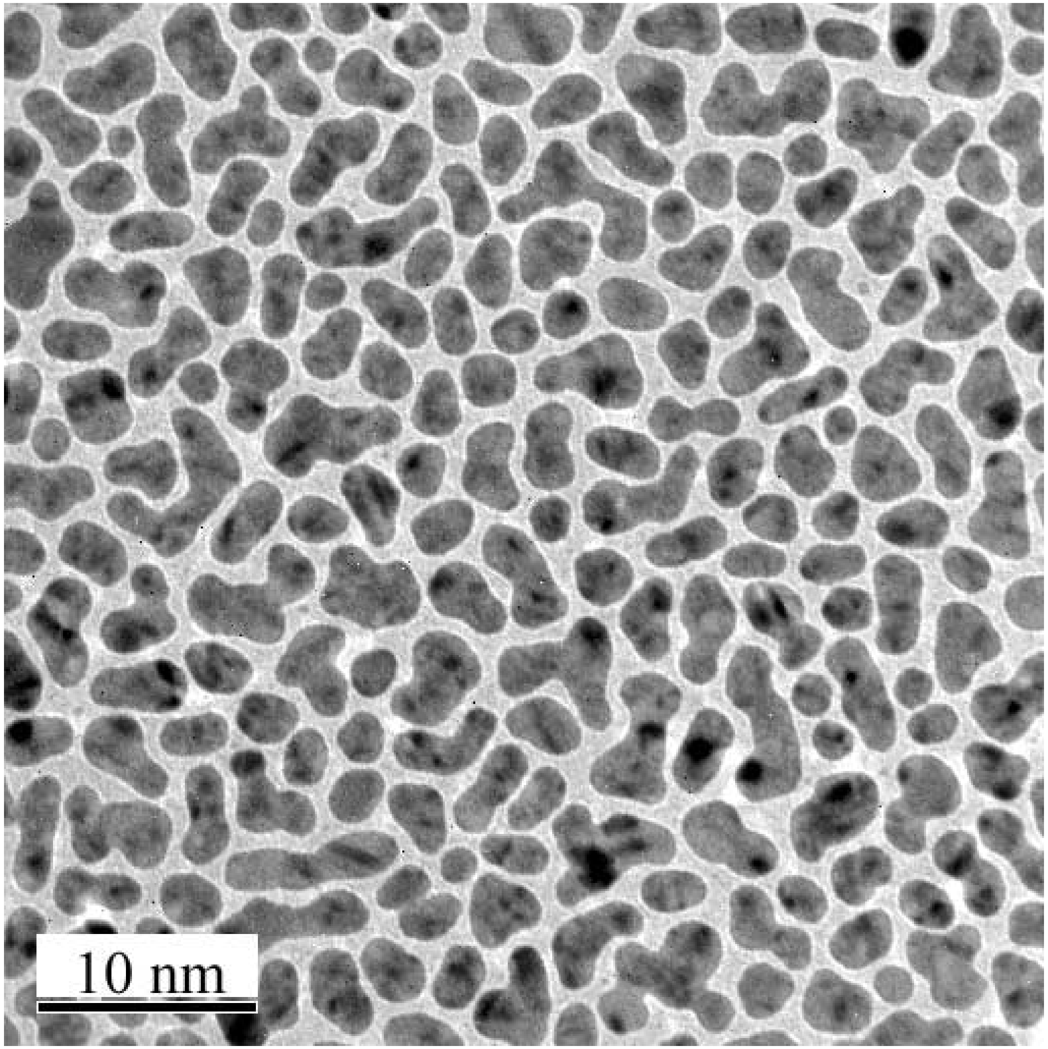
coalesence.gif



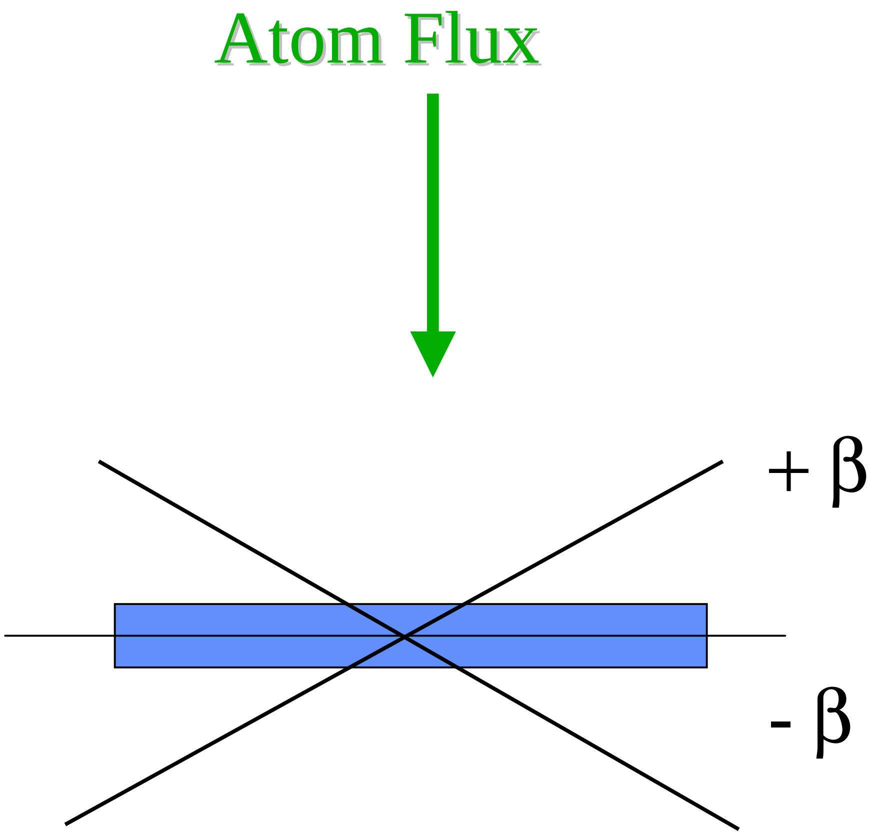
High-resolution TEM video clip courtesy of C. Nelson, National Center for Electron Microscopy, Berkeley, 2003.

Ag on Si_3N_4 - TEM

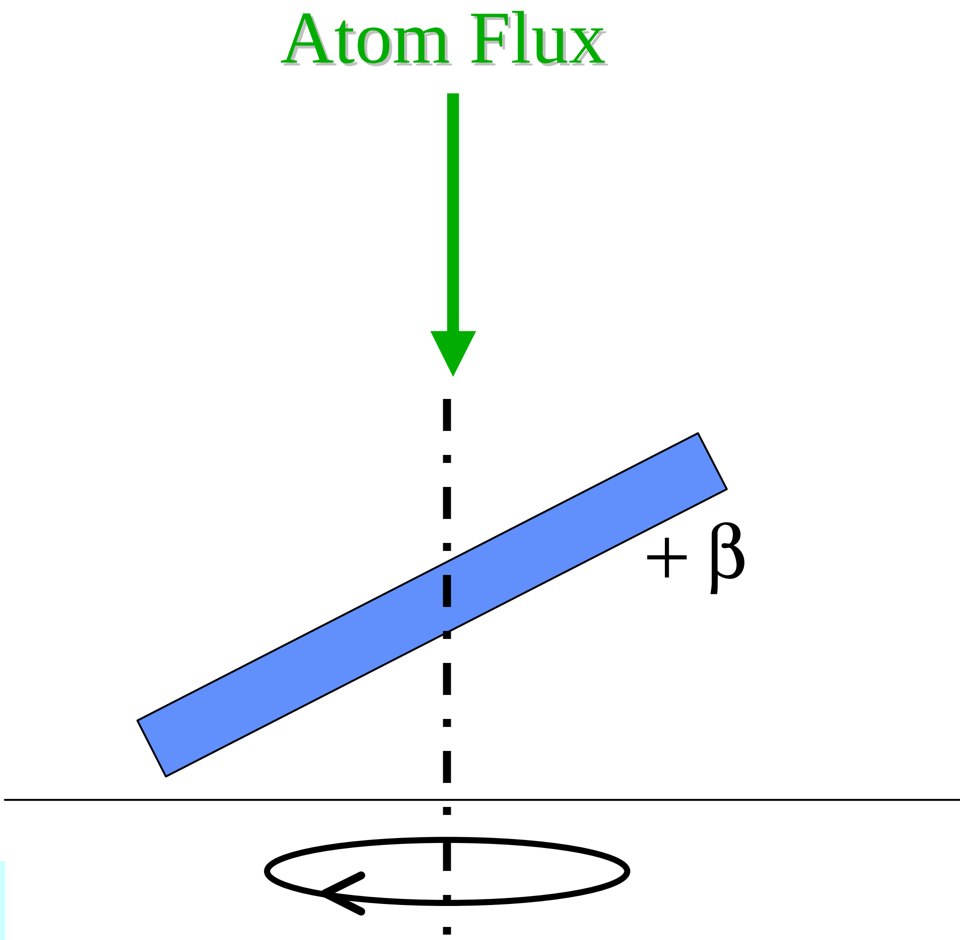
• energetic condensation of Ag ions (about 70 eV/ion)
• ~ 6-8 nm film shows island growth
• "same" film on ZnO shows good electronic conduction hence coalescence has occurred



Sculptured Films: Principle

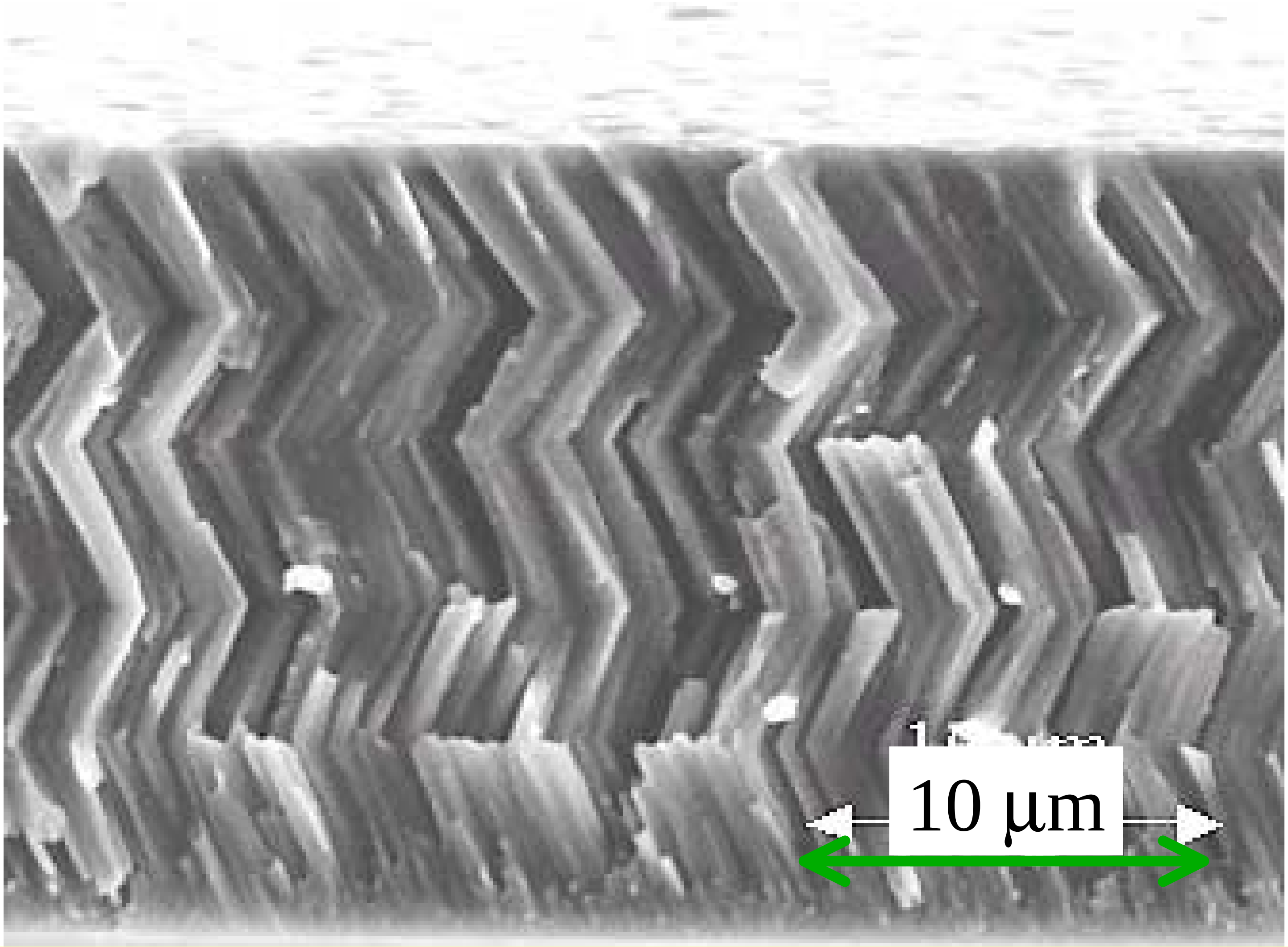


non-chiral sculptures
(can be made compatible with large-area coating)



chiral sculptures

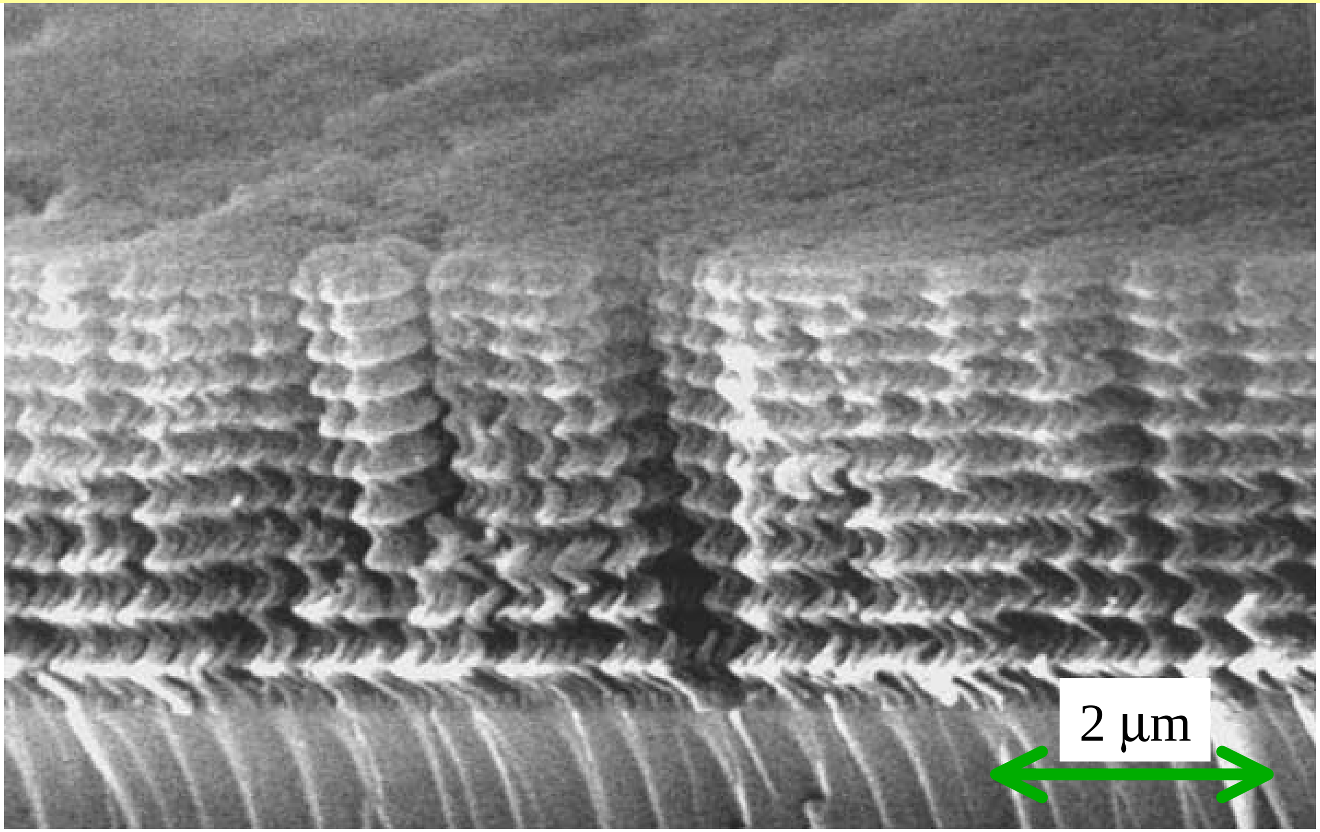
Sculptured Films: Chevrons



O. R. Monteiro, et al., J. Phys. D: Appl. Phys. **31,** 3188 (1998)

Sculptured Films: Helicoidal Bianisotropic Thin Films

10-turn chiral SiO_2 sample made by Paul Sundahl, Penn State University (see also web page of Dr. Akhlesh Lakhtakia and Dr. Russell Messier, Penn State)



- films show optical activity with nematic liquid crystals: determine/ change transmission of polarized light

Transparent Electronics

TCO (transparent conductive oxides)

- optical coating
- “passive” coatings

- used in low and high-tech:
  - solar control coatings
  - antistatic coatings
  - touch display panels
  - solar cells
  - heaters, defrosters
  - RF shields

- “active” transparent electronics

  or

- “invisible” electronics

- used in high-tech, e.g.:
  - AMLCD (active matrix liquid crystal display)

Transparent Electronics

- *n*- *and p*-type material needed demonstrated e.g. for **ZnO**
- wide band-gap: to be transparent
- higher conductivity should be obtained by enhanced mobility thus purer material with less grain boundaries
- great collection of papers: MRS Bull. **25** no 8 (2000)
- if both *n* and *p*-type available, and suitable band structure, light can be emitted or "harvested"

Windows Harvesting Solar Energy?

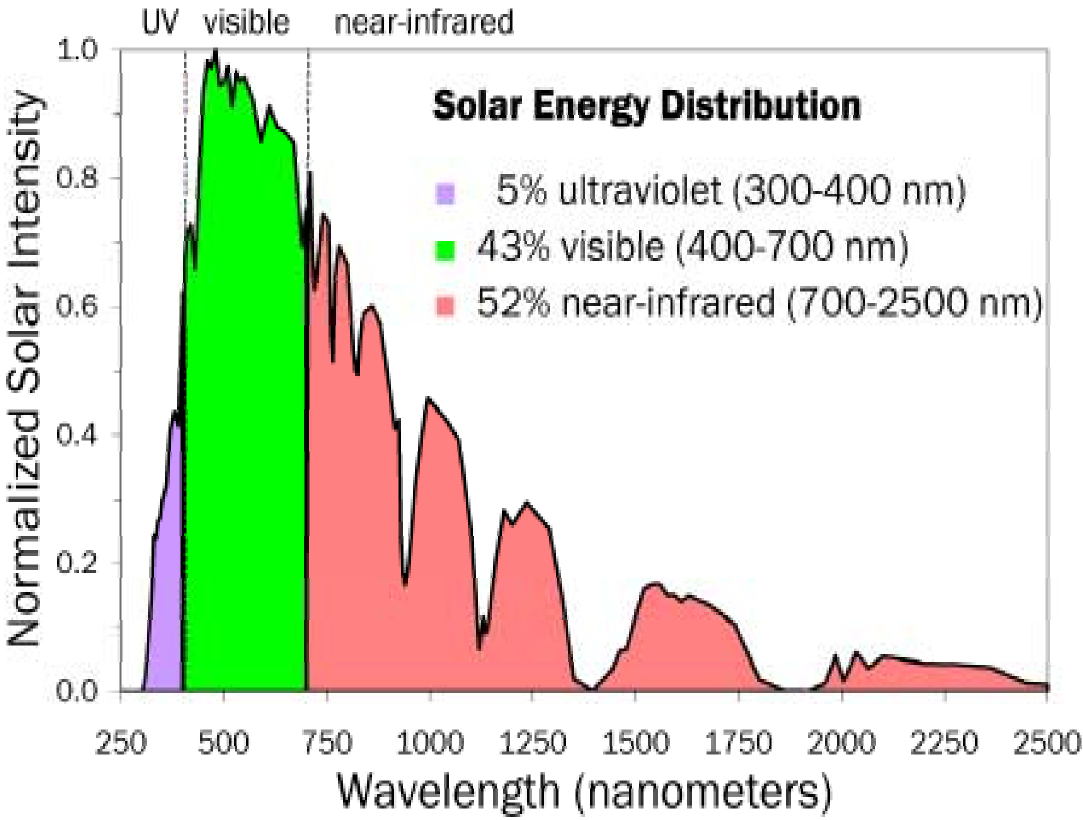
- a principal issue: high transmittance ⟶ a large portion of solar energy cannot be harvested
- is it more likely that façade elements other than windows are used for harvesting solar energy

However, there is hope:

• Windows need to transmit only < 25% when sun brightest

• window does not need to be transparent when room is not occupied

• **if** materials and process economical, harvesting of the IR may be useful

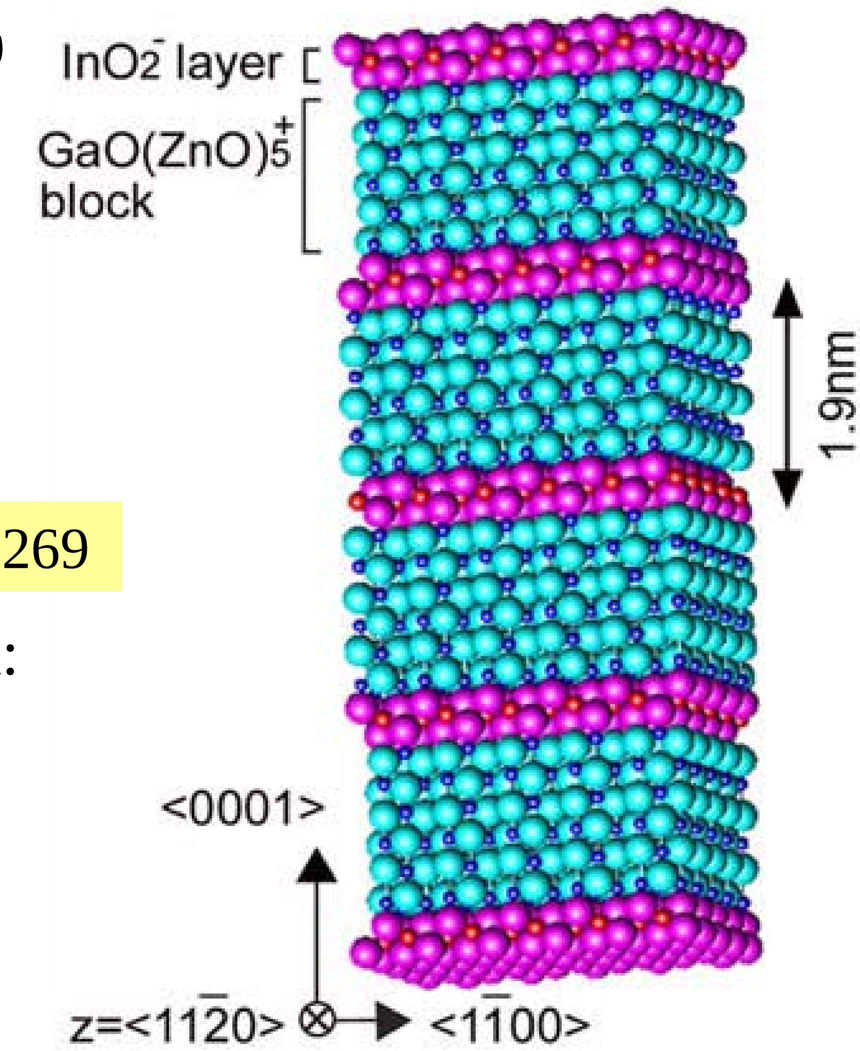


Windows as Areal Lights and Displays ?

• TFET(transparent field effect transistor)
• single-crystalline material: very high mobility demonstrated
• fabrication: PLD with annealing, hence currently not suitable for large areas.

K. Nomura et al., *Science* **300** (2003) 1269

• even if technology issues resolved: cost issues remain!



Summary, Main Conclusions

- Plasma coating on glass is technology older than usually presumed
- Family of sputtering technologies has matured but developments is still very much underway, for example in MF dual magnetron sputtering and pulsed sputtering
- Process and Materials examples:
  - low-E coatings with Ag film: there are thermodynamic and kinetic factors, important for post-deposition dynamics
  - sculptured thin films as nanostructured coatings
  - ZnO as TCO as well as active coating for devices in "transparent electronics"